steam pipes or dangerous electrical conductors. Radiation is always present (background) and is released in substantial quantity by such processes as coal burning and ordinary mining. The International Atomic Energy Agency (IAEA) notes[19] that no serious radiation-induced injury or radiation-induced death has taken place at any nuclear power plant since the first nuclear power reactor went critical in 1956. This is a remarkable record considering that 274 nuclear reactors, representing 2500 reactor-years of operating experience, were in operation in 1982. Coal mining, or even riding in an automobile, is far more hazardous than working in a nuclear establishment. More than 800 nuclear installations around the world have safeguard agreements with the IAEA. This is 98 percent of the nuclear installations outside the nuclear weapons states.

The contamination of gases, liquids, and solids by substances emitting alpha, beta, and gamma radiation are all possible and must be guarded against. Shielding of only a fraction of an inch of ordinary material stops alpha and beta particles, but shielding against gamma radiation and neutrons requires massive quantities of dense materials such as heavy concrete, lead, steel, borosilicate glass, or around 7 m of ordinary water. Of course, shielding is not the only problem, containment must also be considered. Gases must not be allowed to escape, and active materials must remain isolated behind the shields in order for them to be effective. ^{90}Sr and ^{137}Cs (fission fragments) are troublesome because of their moderate half-lives 28 and 30 years, respectively). This is because living organisms tend to concentrate these isotopes selectively from dilute solutions. Unless such materials are excluded from discharge into public waters, they may enter the food chain. This phenomenon is not limited to nuclear isotopes, biological concentration of mercury was the cause of Minimata disease, which led to the outlawing of mercury cell caustic-chlorine manufacture in Japan. Despite these problems, good reliable solutions to the containment problem exist and a recent safety congress[19] concluded "there is no factor relevant to safety that limits the use and development of nuclear power."

WASTE DISPOSAL[20]

The disposal of nuclear waste presents problems, but most are now political rather than technological. Some radioactive materials must be stored for centuries until they decay to harmless materials, others rapidly become harmless.

The volume of waste to be disposed of is surprisingly small. Temporary storage in tanks permits short half-life materials to decay. Liquids can be concentrated or their dissolved solids absorbed in ion-exchange resins, converted into concrete, or glassified, permitting storage in caves, salt mines, deep wells, or the ocean. By removing long-lived isotopes for separate handling, contractors can greatly reduce the storage time for most nuclear waste. It now seems probable that, with proper management, most nuclear wastes will become harmless within 100 years. The quantity requiring geologic storage can be extremely small. The United States does not favor burial at sea because of the possibility of damage to the ecosystem and the expense of deep sea recovery, if necessary. Other countries, however, continue this practice

[19]*IAEA Annual Report*, 1980.

[20]Rochlin, Nuclear Waste Disposal: Two Social Criteria, *Science* 195 23 (1977)

SELECTED REFERENCES

Addinall, E. and H. Ellington: *Nuclear Power in Perspective*, Nichols, New York, 1982.

Advances in Nuclear Science and Technology, vols. 1–13, Plenum, New York, 1981.

Annual Reports to Congress, vol. III, U.S. Department of Energy, DOE/EIA-0173[79]/3. U.S. DOE, National Energy Information Center, Washington D.C., 1980.

"The Clinch River Breeder Reactor Project: a Briefing for Engineers," *Proceedings of the Breeder Reactor Corporation*, April 1975, Information Session, PMC-74-02, CONF-741087, USAEC Technical Information Center, Oak Ridge, Tenn., 1975.

Donnelly: *Major Observations and Conclusions of the Report of the International Fuel Cycle Evaluation (INFCE) and Their Implications of U.S. Non-Proliferation Policy*, Congressional Research Service, Library of Congress, Washington, D.C., 1980.

Dunderstadt, J. J. and L. J. Hamilton: *Nuclear Reactor Analysis*, Wiley, New York, 1976.

Glasstone, S.: *Principles of Nuclear Reactor Engineering*, Van Nostrand, New York, 1955.

Glasstone, S. and A. Sesonske: *Nuclear Reactor Engineering*, Van Nostrand, New York, 1963.

Graves, H. W. Jr.: *Nuclear Fuel Management*, Wiley, New York, 1979.

Knief, R. A.: *Nuclear Energy Technology: Theory and Practice of Commercial Nuclear Power*, McGraw-Hill, New York, 1982.

Lawroski, S. and M. Levenson: *The Redox Process—A Solvent Extraction Reprocessing Method for Irradiated Uranium*, USAEC, TID-7534, Oak Ridge, Tenn., 1957.

Long, J. T.: *Engineering for Nuclear Fuel Reprocessing*, Gordon and Breach, New York, 1967.

Moore, J. G. (ed.): *Scientific Basis for Nuclear Waste Management*, vol. 3, Plenum, New York, 1981.

The National Plan for Radioactive Waste Management, Working Draft 4, U.S. Dept. of Energy, Washington D.C., 1981.

Nuclear Energy Policy Study Group, Nuclear Power Issues and Choices, Ballinger, Cambridge, Mass., 1977.

Rust, J. H.: *Nuclear Power Plant Engineering*, Haralson, Buchanan, Ga., 1979.

Simnad, M. T.. *Fuel Element Experience in Nuclear Reactors*, Gordon and Breach, New York, 1971.

Statistical Data of the Uranium Industry, U.S. Department of Energy GJO-100(80), Bendix Field Engineering Corp., Grand Junction, Colo., 1980.

U.S. Department of Energy, *Technology for Commercial Radioactive Waste Management*, DOE/ET-0028, vols. 1–5, National Technical Information Service, Springfield, Va., 1980.

Villani, S: *Isotope Separation*, American Nuclear Society Monograph, American Nuclear Society, Hinsdale, Ill., 1976.

Weinberg, A. M.: *The Future of Nuclear Power*, Proceedings of the ANS/ENS Topical Meeting on Thermal Reactor Safety, CONF-800403, vols. 1 and 2, American Nuclear Society, LaGrange, Ill., 1980.

Weisman, J. (ed.): *Elements of Nuclear Reactor Design*, Elsevier, New York, 1977.

Chapter 2

Wood-Derived Chemicals

Each year nearly 200×10^6 t of wood are harvested from the nation's forests.[1,1a] Approximately 30×10^6 t are discarded as tree tops, stumps, roots, or scrapped logs. Half of the harvested roundwood is converted into lumber, poles, and similar wood products. The remainder is converted into pulp and paper. Wood processors classify wood into two groups. (1) hardwoods, which come from deciduous trees, and (2) softwoods, which come from conifers. The actual hardness or softness of the wood is irrelevant. Wood is a splendid, renewable resource and very valuable, but waste is enormous. It has been suggested[2] that biomass must be handled like any other valuable product: everything must be sold except the sound of the tree falling. Many new products are technically, but not economically, feasible.

Underutilization of wood products arises from the complexity of the material, lack of integration of chemical, pulp, and lumber companies, disinterest of processing companies in producing and selling by-products, lack of chemical knowledge or interest, and the dilute form in which many of the by-products are available. Since environmental laws have made the stream dumping of pulp-mill waste products impossible, some real interest in waste use has developed, but most such envisioned uses are as fuel. As the price of petroleum products rises, sylvichemicals become more enticing, but the chemistry is more complex than that necessary for petroleum processing. The use of wood as a fuel seems undesirable for such a complex raw material.

The solid portion of wood is over 95% organic.[3] It is a mixture of three groups of polymers: (1) cellulose, which is approximately 45% of the dry weight in an ordered array of high molecular weight glucose polymer chains, currently most valuable as fiber; (2) hemicellulose (20 to 25%) is a disordered array of several sugar polymers for which there is currently no economical use except as fuel; (3) lignin (20 to 25%), which serves as binder for the cellulose fibers, is a complex amorphous polyphenol polymer. Wood also contains extractives—organics removable with inert solvents. These extractives vary with the species and the location in the tree; they vary from 5 to 25% by weight and constitute several classes of chemicals. Table 32.1 shows average values for the composition of U.S. wood. Pentosans are aldopentoses formed by the hydrolysis of high molecular weight polysaccharides.

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[1]t = 1000 kg.

[1a]Goldstein, *Organic Chemicals from Biomass*, CRC Press, Boca Raton, Fla., 1981, Chap. 1.

[2]Myerly, Nicholson, Katzen, and Taylor, The Forest Refinery, *CHEMTECH* 11 (3) 186 (1981).

[3]Browning (ed.), *Chemistry of Wood*, Wiley-Interscience, New York, 1963.

Table 32.1 Composition of Wood

	Softwood,%	Hardwood, %
Holocellulose	66	76
α-Cellulose	46	49
Pentosans	8.5	19.5
Lignin	27	21

SOURCE: *Chemistry in the Utilization of Wood*, Pergamon, Oxford, 1967.

There is a great potential for novel industrial uses for wood, but the chemistry will be difficult. Use as fuel is being urged these days.[4] A ton of green wood or bark generates 18,986 MJ on combustion. Since one of the major problems in wood use is its collection and transportation out of difficult terrain to the place in which it is desired, use of waste wood is particularly attractive at lumber and pulp mills, where these chores are already done. Pulp mills derive over 40 percent of their energy needs from wood residues, and this percentage is increasing. Since the pulp and paper industry is the largest manufacturing consumer of fuel oil, the saving is important.

The derivation of chemicals from wood is an old practice. Potash from wood ashes and tannin from the chestnut tree were mainstays of commerce of the U.S. colonies and the Republic for two centuries.

HARDWOOD DISTILLATION

Charcoal was a valued commodity in antiquity. The ancient Egyptians used the volatile product of hardwood distillation, pyroligneous acid, for embalming. Before synthetic organic chemistry became well established, destructive hardwood distillation provided several important industrial chemicals,[5] among these were acetone, acetic acid, and methanol (still often referred to as wood alcohol). Charcoal is a fine, smokeless fuel, prized for its smokelessness and used extensively for outdoor cooking. Approximately 320,000 t of charcoal are produced yearly in the United States from about 1.4×10^6 t of nonmerchantable wood. Acetone was originally made by the dry distillation of calcium acetate made from wood-derived acetic acid, but better, cheaper sources are available now.

NAVAL STORES

PRODUCTS AND ECONOMICS. The days of wooden ships are past, but the use of pitch and rosin in the navy has attached the name naval stores to the extractable products from various species of pine. Gum naval stores (resin acids, called rosin, and turpentine) are obtained from the gum (oleoresin) collected from tapped pine trees. This labor-intensive source is small and

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[4]Tillman, Sarkanen, and Anderson, *Fuels and Energy from Renewable Resources*, Academic, New York, 1977; Vogt; *Energy Conservation and Use of Renewable Energies in the Bio-Industries*, Pergamon, Oxford, 1981.

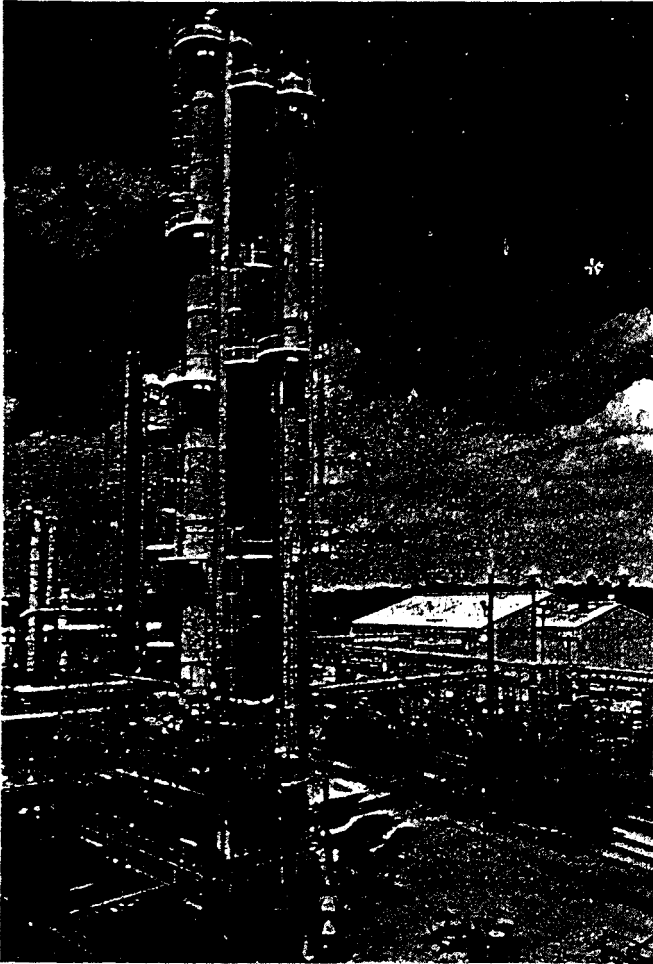[5]Goldstein, op. cit., chap. 5.

Fig. 32.1. Turpentine fractionating complex located in Jacksonville, Fla. This is capable of handling over 36,000 t annually. The basic raw material, crude turpentine from kraft paper mills, is first split into α-pinene and β-pinene. These compounds are then made into many products, such as pine oils, rosin oils, and chemicals for perfume, flavor, and pharmaceutical uses. *(Glidden-Durkee Division of SCM Corp.)*

diminishing. Wood naval stores (rosin and turpentine) are obtained by solvent extraction of pine stumps with inert solvents. Sulfate naval stores (rosin, turpentine, and fatty acids) are obtained from tall oil, a by-product of kraft pulp manufacture (Chap. 33). Resin acids are principally monocarboxylic diterpenes, and rosin is a natural mixture of resin acids. Turpentine is a mixture of monoterpenes. Fig. 32.1 shows a turpentine fractionating complex.

The sources and annual production of naval stores are given in Table 32.2 and Fig. 32.2. The major source is the kraft pulp industry. The annual production of these materials has remained fairly constant for some years, but the end uses of the materials have changed drastically. Figure 32.3 shows a flowchart for naval stores from stumps and gives the usual

Table 32.2 Naval Stores Consumption
(in thousands of metric tons)

|	Turpentine			Rosin		
	1973	1978	1979	1973	1978	1979
Chemicals and rubber	71,364	81,084	81,228	135,558	85,346	83,355
Ester gums and synthetic resins	—	—	—	62,727	54,949	63,172
Paint, varnish, and lacquer	136	106	67	11,818	4,582	5,105
Paper and paper size	182	—	—	81,818	109,273	83,087
Other	590	1270	1,009	12,273	21,105	16,1901
Total	72,272	82,460	82,304	304,194	275,255	250,909

SOURCE: *U.S. Agricultural Statistics, 1981.*
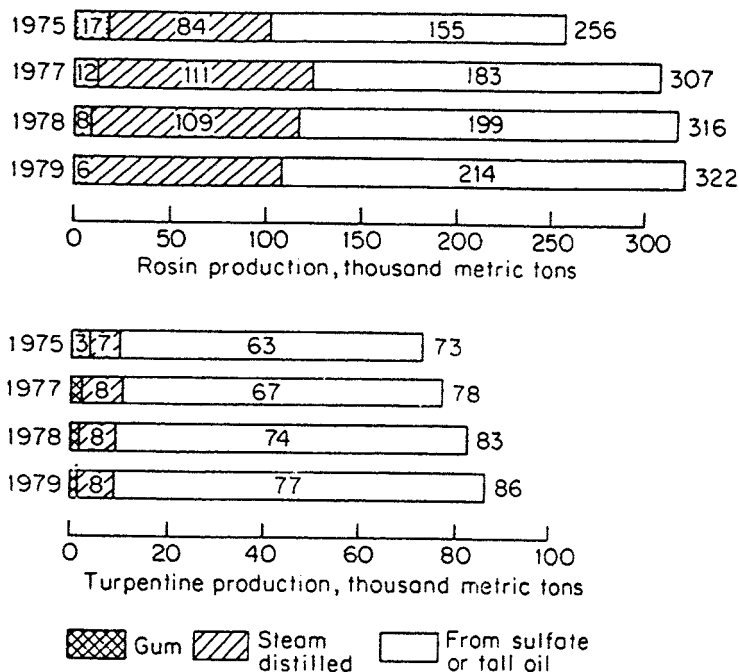
Fig. 32.2. Naval stores production.

distribution of products. Naval stores were exported to England as early as 1608, coming originally from New England, but rapidly replaced by North Carolina and Georgia. Florida and Georgia are presently the major producers of gum turpentine, but compared with other sources, gum production is small. Tall oil is now the major source.

MANUFACTURE OF NAVAL STORES

Gum Oleoresins. Gum is obtained from the pine trees by cutting (slashing) them and sometimes by treating the slashes with chemicals, and then collecting the exuded oleoresin by hand, a slow and expensive process. Separation is by steam distillation.

Steam and Solvent Process. Cut-over pine forest stumps and trash wood provide the raw material. Figure 32.3 shows the essential steps:

The wood is first ground in a wood hog and then reduced to splinters in a shredder.

The chips are loaded into a battery of extractors, where they rest upon a false bottom, below which live steam under pressure is admitted at the end of the run for solvent recovery. The extractors are built of acid-resistant stainless alloys and operate at pressures of 446 to 584 kPag.

The solvent (so selected that it is easily separated from turpentine) countercurrently extracts the chips. This solvent may be naphtha or a petroleum fraction with a boiling range of 93 to 116°C. The hot solvent is drained off, and the residual material on the chips is removed by subsequent steam distillation. The chips are used for fuel.

Most of the solvent is removed from the turpentine, pine oil, and rosin in a concentrating evaporator.

The residue from the first evaporator is sent to an intermediate evaporator. The vapors from this evaporator are led into the upper part of the continuous fractionating column, and the residue is sent to the finishing evaporator.
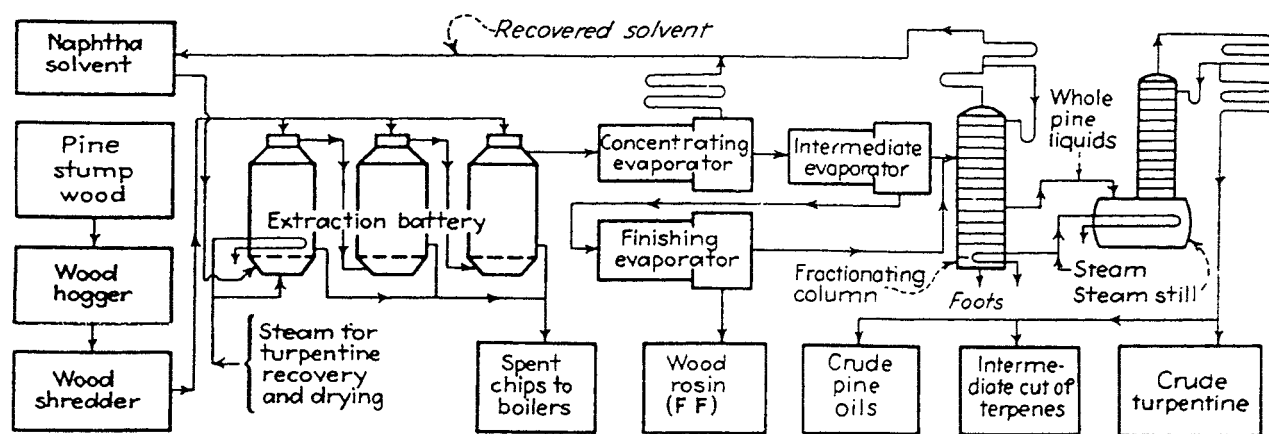
From 1000 t of white pine can be obtained (in liters):

Turpentine, 155–167°C	21,910	Pine oils	20,790
Intermediate turpene*	11,230	Tar	2,250
		Total crude oils	56,185

*Included herein are the hydrocarbons: p-menthane, dipentene, p-cymene, terpinene, and terpinolene.

Fig. 32.3. Flowchart for wood rosin and turpentine production by steam and solvent extraction.

Vapors from this final evaporator are combined with those of the intermediate evaporator before entering the fractionating column.

Residue from the third evaporator is whole-wood rosin and may be treated by selective solvents and certain absorbents such as fuller's earth to yield light rosins.

The continuous fractionating column separates the pine oils and turpentine from the last of the solvent. Pine liquids from the continuous column are separated into three fractions in a batch still: crude pine oil, an intermediate cut of terpenes, and crude turpentine. Careful fractionation of these three cuts produces many marketable products.

TURPENTINE. Turpentine is a mixture of organic compounds known as terpenes. An example, and a major constituent, is α-pinene.[6]
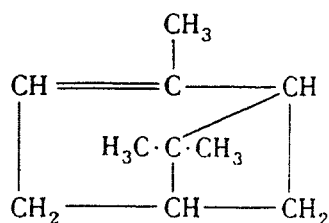
Originally used as a volatile paint and varnish thinner, but undesirable because of its strong odor, turpentine has been almost totally replaced by volatile petroleum fractions (VM&P, varnish maker's and painter's naphtha). Violent swings between shortage and oversupply have hampered the industry.

[6]Terpenes, ECT, 2d ed., vol. 14, 1969, p. 803.

SULFATE PULP TURPENTINE. The relief gases from the digesters for kraft (sulfate) pulp contain turpentine and pine oil. When the gases are condensed, 8 to 40 L of oil can be separated per ton of pulp produced. This oil contains 50 to 60% turpentine and 10 to 20% pine oil; these are usually separated by distillation. Odoriferous mercaptans contaminate the turpentine. Treatment with mild oxidizing agents, such as sodium hypochlorite, or solution in ethylene-diamine removes these substances.

Pine oil can be obtained by fractionating pine stump extractives, but about half is "synthetic," made by mineral acid conversion of the α-pinene in turpentine to α-terpineol. Further treatment gives the pharmaceutical, terpin hydrate. Pine oil is an odorant and bactericide in household cleaners, an odorant for a variety of other products, and a flotation agent; it is also used in processing textiles.

Low molecular weight polyterpin resins used in pressure-sensitive tapes, adhesives, chewing gum, dry-cleaning, and paper sizes are made from α- and β-pinenes and pyrolyzed α-pinene from turpentine.

Toxaphene, a valuable pesticide, has been made by chlorination of a terpene obtained from turpentine. Its use has recently been severely restricted.

A wide variety of flavors and fragrances is made by the isolation of fractions of turpentine and by chemical conversion of these fractions. These include lime, lemon, peppermint, spearmint, and nutmeg synthetic essential oils and linalool, citronellol, nerol, geraniol, menthol, and ionones as semisynthetics.[7] Some entirely new fragrances and flavors have also been prepared. Turpentine is much more valuable as a chemical raw material than it ever was as a solvent.

ROSIN. Rosin is obtained from both stump extract and tall oil processing. The availability of aged stumps is steadily diminishing and with it the competition for tall oil rosin. The demand for tall oil rosin, 220,000 t in 1979, is expected to expand to 283×10^6 t by 1989.[8] Rosin contains mainly diterpene resins such as abietic and pimaric. Rosins are generally modified before use by means of hydrogenation, esterification, reaction with formaldehyde or maleic acid, and similar processes. The use of the sodium salt of rosin in yellow laundry soap has largely disappeared. The major use is as a paper sizing agent as the precipitated aluminum salt. Esterified, it becomes ester gum, an ingredient of some varnishes. Rosin is also used in tackifiers, adhesives, chewing gum, and coatings.

TALL OIL. Tall oil is the generic name for the oil obtained upon acidification of the black liquor residue from kraft digesters. Kraft processing dissolves the fats, fatty acids, rosin, and rosin acids contained in pine woods in the form of sodium salts. When the black liquor is concentrated to make it possible to recover some of its chemical and heating value, the soaps become insoluble and can be skimmed off. The brown, frothy curd thus obtained is then made acidic with sulfuric acid,[9] converting the constituents to a dark-brown fluid called tall oil. The name is derived from the Swedish "talloja," pine oil, and has come into use to avoid confusion with pine oil from wood distillation, already an article of commerce. Fractionation under

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[7]Zinkel, Chemicals from Trees, *CHEMTECH* 5 (4) 238 (1975).

[8]Naval Stores Markets on Hold during Recession, *Chem. Eng. News* 60 (21) 30 (1982).

[9]Continuous Tall Oil Route Saves on Power and Labor, *Chem. Eng.* 79 (2) 76 (1972); How to Increase Tall Oil Output, *Chem. Eng. Prog.* 69 (9) 80 (1973); Drew, Maximizing Tall Oil Recovery, *Chem. Eng. Prog.* 72 (6) 64 (1976).

vacuum separates the crude material into its component parts. Tall oil fatty acids have enjoyed a brisk sale because, among other good properties, they are the cheapest organic acids available. United States tall oil fractionating capacity was 860,000 t/year in 1982.[10] Utilization of this material reduces waste and stream pollution. Fractionation allows for various desired compositions. Tall oil is the major source of turpentine. Tall oil fatty acids are mostly normal C_{18} acids, 75% mono- and di-unsaturated, with lesser amounts of saturated and tri-unsaturated constituents. Alkyd resins are the major market (20 percent) for tall oil, and soybean oil is its major competitor. Seven to ten percent is used in soap manufacture. There are a host of other uses, waterproofing agents, dimer acids, polyamide resins for printer's ink, adhesives, detergents, and agricultural emulsifiers, to name a few. Price is around 45 cents per kilogram.

LIGNINS AND LIGNOSULFONATES. Lignin constitutes a large percentage of the noncellulosic part of wood. Newer laboratory processes yield quality lignin with molecular weights of 200 to 1000, but kraft process lignin has a molecular weight of 1000 to 50,000 and is altered chemically by sulfonation. For years it has been realized that this should be an important source of benzenoid chemicals, but development has been slow in coming.[11] Presently it is mostly used as a fuel, but as petroleum becomes increasingly scarce and expensive, proposals and experimental plants for using this material begin to appear. One such process[12] uses fluid-bed hydrocracking and dealkylation to produce phenols and benzene

Lignin derivatives, sulfonated alkali lignin and sulfite lignosulfonates, are being used to increase tertiary oil recovery in "pumped out" oil wells,[13] replacing more expensive synthetic detergents. This could become a very large market.

High yield pulping processes and improved bleaching methods leave much more lignin in paper, which is certainly one of its most economical applications. Lignin's composition and molecular weight vary with the species of wood being used. Chemical technology concerning the fragmentation of large molecules to produce useful small ones is not nearly so well-developed as that for synthesis of large molecules from small ones. This impedes progress in finding economical processes for using lignin.

Despite these difficulties, several products made from lignin are currently profitable. Vanillin is made from sulfite waste liquor, but the available supply greatly exceeds the demand despite low yields. Dimethyl sulfide, dimethyl sulfoxide (DMSO), and methyl mercaptan are finding small but important markets. Alkaline waste liquors and lignosulfonates are sold as dust stabilizers, asphalt emulsion stabilizers, dispersing agents, binders for various substances, drilling fluid additives, etc., but the major use remains as fuel for pulp mills.

HYDROLYSIS OF WOOD

Wood, waste paper, and municipal waste contain cellulose which can be converted to sugar which can then be fermented to give ethanol, a potentially important motor fuel. This process

[10]Turmoil in the Market for Tall Oil Derivatives, *Chem. Week* 129 (12) 29 (1981). Layman, Naval Stores Markets on Hold during Recession, *Chem. Eng. News* 60 (21) 30 (1982).

[11]Sarkanen and Ludwig, *Lignins*, Wiley-Interscience, New York, 1971; Graff, *Chem. Eng.* 89 (26) 25 (1982).

[12]Lignin Conversion Process Shows Promise, *Chem. Eng. News* 58 (44) 35 (1980).

[13]Wood Chemicals Inject New Life into Tired Oil Wells, *Chem. Week*, 124 (25) 65 (1979).

continues to attract attention because it utilizes waste materials instead of foodstuffs for its raw materials. The process was first developed in Germany during World War I and has been under development ever since. By 1941, 30 foreign plants were in successful operation producing alcohol from wood by hydrolysis with weak sulfuric or hydrochloric acid, followed by fermentation. The U.S.S.R. has a number of operating plants. Cellulose is considerably more valuable (44 cents per kilogram) than glucose (7 cents per kilogram) or ethanol, so only sources unsuitable for paper production can be considered as raw material. Straw, sawdust, corncobs, etc., are possibilities.

Until recently, most studies showed all processes suggested to be uneconomical in the United States. The increases in petroleum costs have revived interest and it appears that financially competitive processes are about to emerge.[14] The processes are in a state of flux, as described in the references, and the definitive commercial process is not yet determined.

Hydrolysis to glucose can be accomplished with weak or strong sulfuric or hydrochloric acids or with any of several enzymes which work under both high and low temperatures on separated or unseparated cellulose. Conversion of the cellulose present varies from 50 to over 90 percent, and the time required for conversion is highly variable. The final alcohol solution obtained before rectification varies from 2% to around 12%. To keep processing costs within reason, at least 5% is required. Getting hydrolyzing reagents to react with wood involves effective contact with the whole mass, so pressure systems and wood explosion techniques involving screw presses are being tried. By-product utilization is also important. Molasses for cattle feed and lignin suitable for use in plastics are to be produced, and some proposed installations are designed to only make such syrups and solids instead of ethanol. It would be very desirable to convert hemicelluloses to fermentable sugars, and some processes can do this. Figure 32.4 shows a flowchart for a currently demonstrated process designed to make dilute alcohol (commonly referred to as beer).

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[14]Hsu, Ladisch, and Tsao, Alcohol from Cellulose, *CHEMTECH* 10 (5) 315 (1980); Emert and Katzen, Gulf's Cellulose to Ethanol Project, *CHEMTECH* 10 (10) 610 (1980); Emert, Katzen, and Kaupisch, Economic Update on the Gulf Cellulose Alcohol Process, *Chem. Eng. Prog.* 76 (9) 47 (1980); Remirez, Wood-to-Ethanol Methods Edge Closer to Fruition, *Chem. Eng.* 88 (2) 51 (1981); Berry, Ethanol from Wood, *Chem. Eng.* 88 (12) 62 (1981); Worthy, Cellulose-to-Ethanol Projects Losing Momentum, *Chem. Eng. News* 59 (49) 35 (1981).
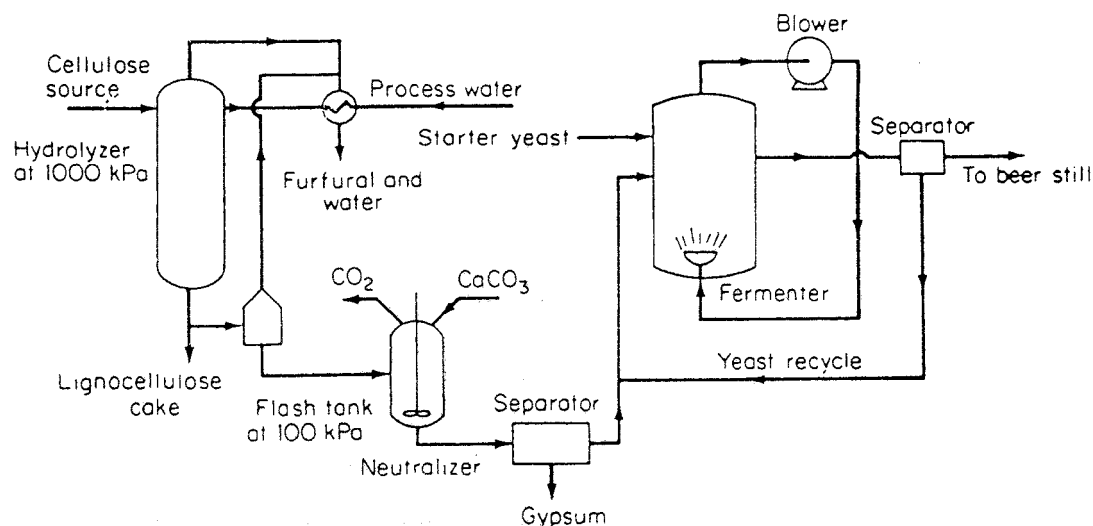

Fig. 32.4. Ethanol from wood.

Hardwoods, when used to make paper by the sulfite process, yield waste liquors containing as high as 3% sugars, principally xylose and arabinose, softwoods give only about 2% sugars, principally mannose along with mixed hexoses and pentoses. After the sulfite content of the waste liquor is reduced by steam stripping, $(NH_4)_2HPO_4$ is added to promote growth of yeast, the pH is adjusted, and the mixture added to a continuous fermenter inoculated with *Candida utilis* (also known as *Torulopsis utilis*) yeast. Aerobic fermentation ensues, controlled at 32 to 38°C by cooling coils or an exterior heat exchanger. Much foaming occurs. The fermenters are large, 8 m in diameter × 4.3 m high. Fermenter liquor containing about 1% yeast solids is removed at the same rate at which feed is added and concentrated to 5% by centrifuging. Repeated washing and centrifuging gives a solids content of 15%. This material is then pasteurized and dried in spray or drum driers. The material thus obtained is called torula yeast and contains about 47% protein and a very high vitamin content. It makes an excellent dietary supplement for animal feed, quite comparable with milk and meat.

In the sulfite process for the manufacture of pulp, sugars are formed by the hydrolysis of wood constituents that are dissolved out when producing usable fibers for paper. Approximately 65 percent of these sugars is capable of being fermented to alcohol. This is equivalent to about 1 to 2 percent of the sulfite waste liquor. First, the sulfite waste liquor is separated from the pulp and conditioned for fermentation.[15] After cooling to 30°C and adding lime (to adjust the pH to 4.5) and urea nutrient, the liquor is pumped into the fermentors and fermented. The alcohol is distilled out and rectified. In Sweden all the alcohol (and many derivatives therefrom) is based on waste sulfite liquors, including all beverage spirits and, during the war, alcohol for motor fuel.

Xylose and xylitol are being made from wood and have found a small market as sweeteners for diabetics.

WOOD EXTRACTIVES
AND CONVERSION PROCESSES

Wood is the source of a large number of chemicals and pharmaceuticals, many of them produced primarily outside the United States. Tannins extracted from chestnut and oak wood, bark, and leaves were of major importance until the chestnut was destroyed by blight and the oak proved too expensive to collect. Cedarwood oil continues to be used for "cedar" chests and sassafras oil is used for flavoring. Several essential oils from twigs, barks, and fruits enjoy brisk but small sales. Gums are also obtained from a variety of trees such as tara and locust. Only one, arabinogalactan, a water-soluble gum from the western larch or tamarack *(Larix occidentalis)* is made in the United States in any quantity. Rubber is a well-known forest product. Several different trees yield oils and waxes that are articles of commerce; jojoba oil and carnauba wax are probably the best known. Quinine is from cinchona bark. Furfural is made by alkaline treatment of wood, oat hulls, or corncobs. There are a variety of spices produced in small quantities for specialty trades which are rarely thought of as chemical products.

Bark removed from trees at sawmills and pulpmills is regarded as an expensive nuisance. Some inexpensive fillers are made from bark flour, but most is burned, used as a soil improver.

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[15]*Forest Products and the Environment*, AIChE Symp. Ser. No. 133, Vol. 69, 1973, p. 2

or wasted. A plant in Oregon[16] converts fir bark into a high-quality vegetable wax, a thermosetting-resin extender, and a phenol substitute. Cork and bast fiber can also be made. Much more extensive use of bark and wood by-products must be made in the future. Wood products should not be regarded primarily as fuels.

CELLULOSE DERIVATIVES

The most important cellulose products are pulp and paper, so Chap. 33 is devoted to their manufacture.

Rayon, an excellent polymer of regenerated cellulose, is covered in Chap. 35 under synthetic fibers.

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[16]Good and Trocino, Fir-Bark Conversion Route, *Chem. Eng.* 81 (11) 20 (1974); Burgon et al., U.S. Patent 2,880,216.
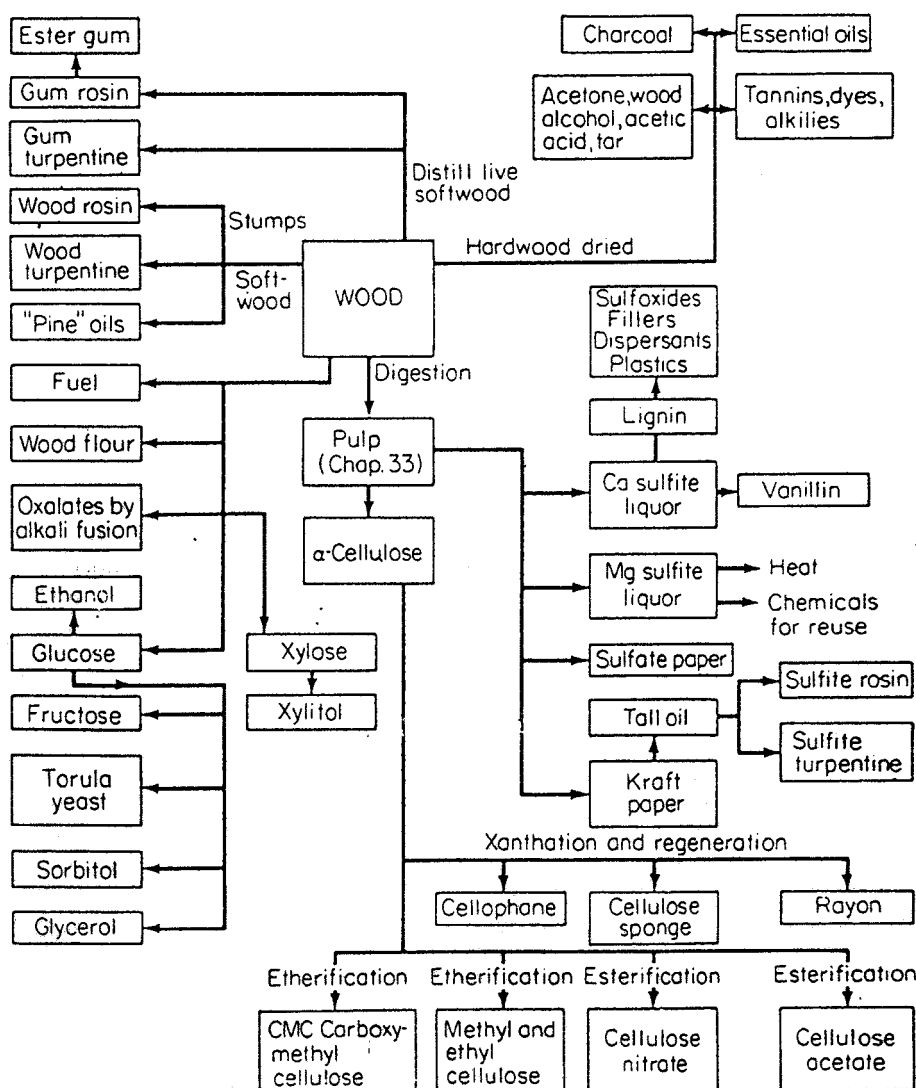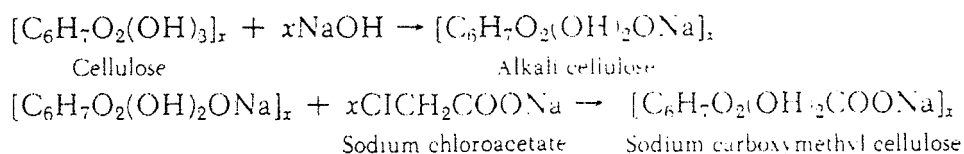

Fig. 32.5. Wood chemicals.

Highly purified cellulose, known as α-cellulose, is the basic material for the manufacture of cellulose nitrate for plastics and explosives as well as most chemical derivatives.

Many cellulose derivatives have attained commercial importance (Fig. 32.5) such as the ethers: ethyl cellulose, methyl cellulose (Dow's Methocel), and carboxymethyl cellulose. The last mentioned is frequently known as CMC and may be prepared by the following alkylation:

$$[C_6H_7O_2(OH)_3]_x + xNaOH \rightarrow [C_6H_7O_2(OH)_2ONa]_x$$
Cellulose   Alkali cellulose

$$[C_6H_7O_2(OH)_2ONa]_x + xClCH_2COONa \rightarrow [C_6H_7O_2(OH)_2COONa]_x$$
Sodium chloroacetate   Sodium carboxymethyl cellulose

Various degrees of etherification have been commercialized. Sodium CMC is a white powder when dry, though it is generally produced and sold as solutions of varying concentration and viscosity. By 1970, CMC production had grown to more than 30×10^6 kg/year. It is physiologically inert and is employed as a protective coating for textiles and paper, for sizing, for ice cream and other emulsion stabilizers, and as an additive to impart strength to sausage casings and other films. Hydroxyethyl cellulose, a high-viscosity product, is useful as a thickener and a protective colloid in water-based coatings.

Among the many specialty products developed, cellulose sponges form an important segment. The dyed viscose cellulose sponge syrup is mixed with various-sized crystals of sodium sulfate, placed in a mold, and heated to "set" the mix around the crystals. Further heating dissolves the crystals in water (that is part of their own crystallization), after which the product is removed from the mold and washed.

SELECTED REFERENCES

Browning, B. L. (ed.): *Chemistry of Wood*, Wiley-Interscience, New York, 1976

Frederick, W. J. (ed.): *New Process Alternatives in the Forest Products Industries*, AIChE Symposium Series 76, No. 200, 1980.

Gould, R. F. (ed.): in "Wood," *Literature of Chemical Technology*, ACS Monograph, 1966, chap. 21

Hillis, W. E. (ed.) *Wood Extractives*, Academic, New York, 1962

Lightsey, R. R. (ed): *The Role of Chemical Engineering in Utilizing the Nation's Forest Resources*, AIChE Symposium Series 76, No. 195 (1980).

Maloney, G. T.: *Chemicals from Pulp and Wood Waste-Production and Application*, Noyes, Park Ridge, N.J., 1978.

Oshima, M.: *Wood Chemistry (Foreign Processes)*, Noyes, Park Ridge, N.J., 1965

Pearl, I. A.: *Chemistry of Lignin*, Marcel Dekker, New York, 1967

Pinder, A. R.: *Chemistry of the Terpenes*, Wiley, New York, 1960.

Venkatesh, V. (ed.): *Advances in the Utilization and Processing of Forest Products*, AIChE Symposium Series 75, No. 184 (1979)

Wilke, C. R. (ed.): *Cellulose as a Chemical and Energy Resource*, Wiley-Interscience, New York, 1976

Zachary, L. G., H. W. Bajak, and F. J. Eveline (eds.): *Tall Oil and Its Uses*, Pulp Chemicals Assoc., 1965

Chapter 3

Man-Made Fiber and Film Industries

HISTORICAL. Fibers were originally of natural origin and were produced from wool, silk, cotton, flax, and similar materials. The first man-made fibers were made by Swan in 1883 when he squirted a solution of cellulose nitrate in acetic acid through holes. The first commercial fibers made from cellulose nitrate were produced by Chardonnet who patented his process in 1885. The next synthetic fiber was also a cellulose derivative, regenerated cellulose or viscose. Although the production of viscose was patented in 1892, it was not until 1930 that the world production had grown to 200,000 t annually.[1] This was due, in part, to the poor wet strength of the original fibers. Viscose was considered to be a cheap, poor substitute for silk until methods of increasing the wet strength were developed. Other variations of cellulose fibers were invented and introduced. Cuprammonium rayon fiber was made about 1900, and cellulose acetate fiber about 1921. Many improvements and variations have been made on these basic cellulose fibers.

The first truly synthetic fiber was nylon (a polyamide) introduced in 1940. This was discovered by Carothers and was commercialized by DuPont. The next fibers that emerged were polyesters, acrylics, and polyolefins. These four types were the principal synthetic fibers produced until the middle 1950s. During the latter part of the 1950s, and continuing to today, much research was devoted to improving the properties of the fibers and to development of fibers with special properties for particular uses (e.g., high-temperature resistant fibers).

USES AND ECONOMICS. Man-made fibers, from their humble beginning, have grown to 45 percent of the world's fiber production. In 1981, 14×10^6 t of man-made fibers was produced worldwide, and natural fibers prepared amounted to 17×10^6 t. The production of the various fibers in the United States from 1966 to 1981 is shown in Fig. 35.1.

The uses of man-made fibers depend upon the nature of the individual fiber. Clothing, carpets, and upholstery are all made largely, or wholly, of synthetic fibers. The blends of polyester and cotton have imparted ease of washability and permanent-press to shirts and other garments. Most of the nylon produced in the United States is used for carpets. Other uses will be discussed in connection with the individual fibers.

PROPERTIES OF FIBERS. Three of the more important general properties of fibers are length, crimp, and denier. Fibers are either a continuous filament or short fibers, rather uniform in length, spun into a thread. The short fibers, i.e., cotton and wool, are called staple. Continuous filaments can be of almost infinite length and most synthetic fibers, as well as natural silk, are of this type. Synthetic staple fibers are prepared by cutting continuous filaments to short, uniform lengths, usually between 3.5 and 15 cm.
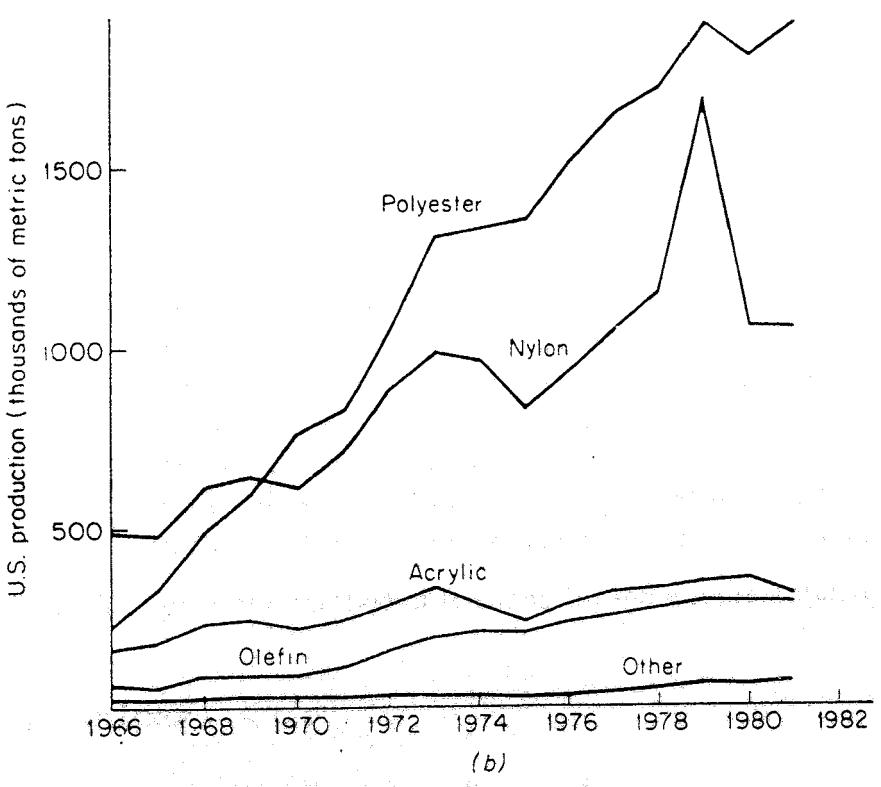
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[1] t = 1000 kg.

Fig. 35.1. Trends in the production of man-made fibers.